Transient Second Harmonic Generation from Oxazine Dyes at the Air/Water Interface

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Abstract

Ultrafast surface second harmonic generation (SHG) studies are reported for several oxazine dyes at the air/water interface. As we demonstrated previously [*J. Phys. Chem. B* **2001**, *105,* 3062] in our steady-state SHG studies of aqueous oxazine dye solutions, the SHG signals are almost entirely due to dimers. The transient SHG recovery is biexponential with time constants of 4-8 ps and 22-44 ps depending on the dye and the solution composition. Transient absorption measurements for bulk dye solutions of water and methanol and the results indicate a fast (2 ps) solvation dynamics component as well as a longer component due to the excited-state lifetime (>400 ps). The SHG recovery is single-photon resonant and is attributed to two parallel ground state recovery mechanisms, restricting the possible explanations for the observed decay times. The shorter SHG decay time (~5 ps) could be due to ground state solvent relaxation, while the intermediate decay time (~25 ps) mostly likely results from vibrational relaxation of "hot" ground state aggregates after internal conversion (IC) / intersystem crossing (ISC). The two decay times are different than what is seen for bulk solution and they resemble what has been previously reported for dye aggregates.

Introduction

Why Study Interfaces?

Interfaces are involved in many physical / biological / atmospheric systems

Compared with isotropic (bulk) environments:
- Are interfaces unique? If so, how?
- Are microscopic and macroscopic properties altered similarly?

Why Study Dye Aggregates?

Industrial Applications
- Photography, photovoltaic cells, light harvesting devices

Dye Aggregates are a sensitive probe of environment
- Laser dyes are well characterized in the bulk
- Dye aggregates are more prevalent at the air/water interface than in the bulk (IR125, Levinger, 1995)

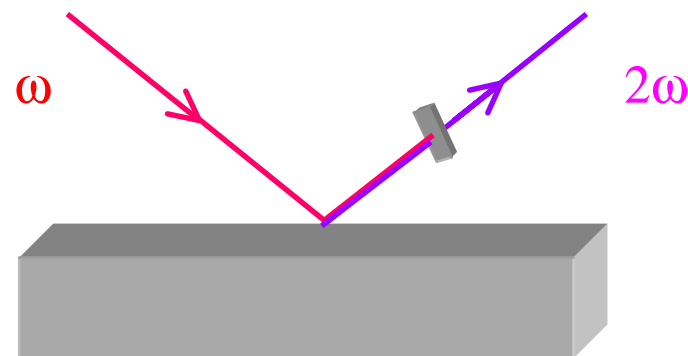# Second Harmonic Generation at the Air/Water Interface

Nonlinear surface spectroscopy:

Detects molecules only at the interface

Second Harmonic Generation (SHG)

ω 2ω

$$I(2\omega) \propto |\chi^{(2)} I(\omega)|^2$$

$$\chi^{(2)} = N_s <T> \beta$$

Previous SHG and Sum Frequency Generation studies of
air/liquid (& liquid/liquid) interfaces:

Steady state (spectra; IR & UV/VIS) > dynamics (VIS)

Steady state	Dynamics
pH, pK	rotational reorientation
adsorption free energy (ΔG_{ads})	isomerization
surface polarity	

SHG from Oxazine Dyes at the Air/Water Interface

Steady-state SHG Studies - study equilibrium properties:

- Electronic Structure: I_{SHG} vs. λ spectra

- Surface K_d and ΔG_{ads}: I_{SHG} vs. bulk dye concentration

- Composition: dependence on bulk salt, surfactant, other solvents

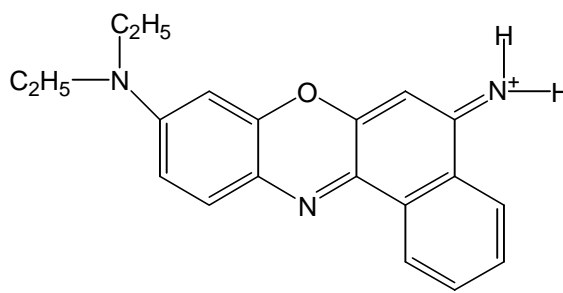- Aggregate orientation at interface: anisotropy (I_{SHG} vs γ)

Dynamics Studies

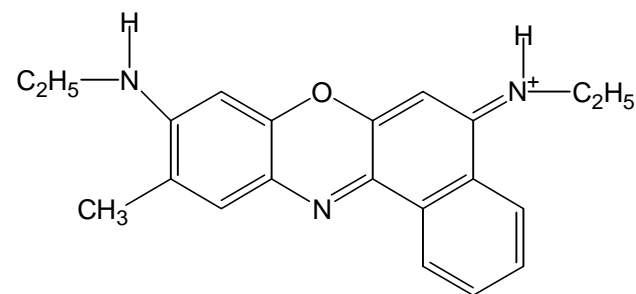Visible pump - probe transient absorption of bulk dye solutions

Visible pump - SHG probe of the dyes at the air / water interface
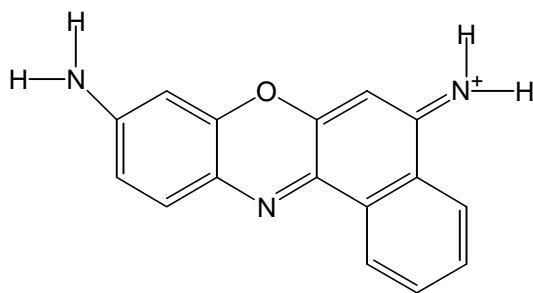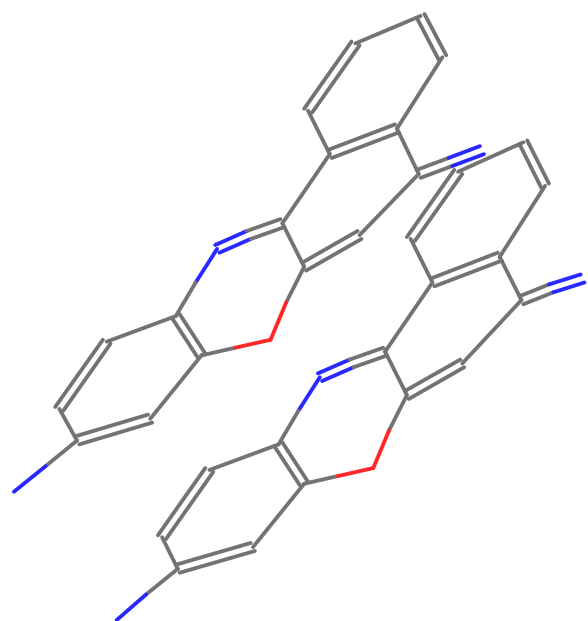
Cresyl Violet

Nile Blue

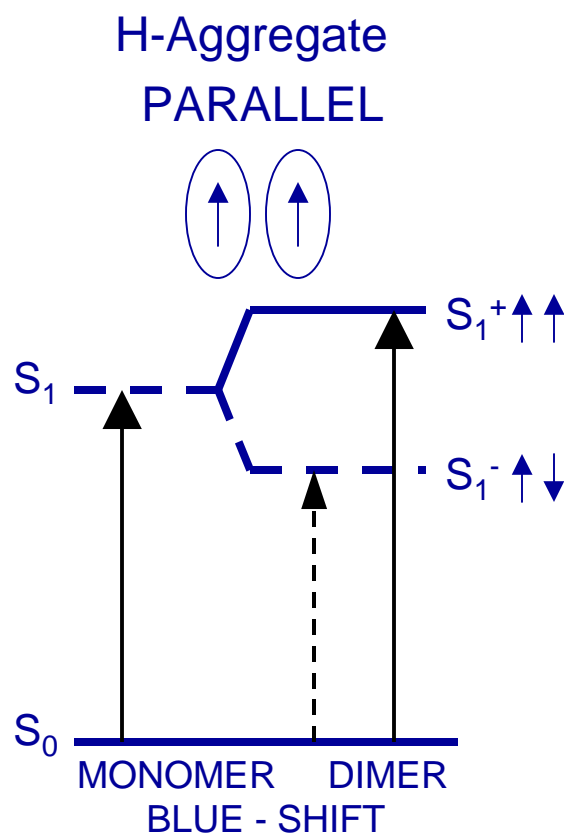Oxazine 720

H-Aggregate Dimer Electronic Structure

Exciton theory of dipole - dipole coupling (Kasha, 1958)

Coupling depends on distance and relative orientation of monomers

Electronic level splitting - spectral shift of aggregate absorption
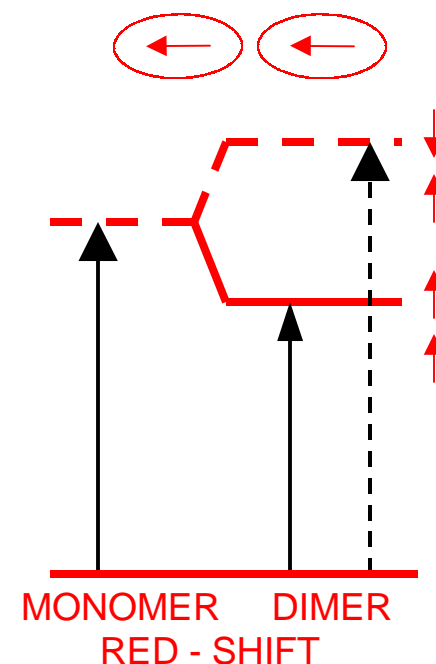
From Kasha, 1976

H-Aggregate
PARALLEL

$S_1^+ \uparrow\uparrow$

S_1

$S_1^- \uparrow\downarrow$

S_0

MONOMER   DIMER
BLUE - SHIFT

J-Aggregate
HEAD-TO-TAIL

MONOMER   DIMER
RED - SHIFT

Cresyl violet
H-Aggregate

Results from Bulk Solution Absorption Spectra

Agreement with previous results for K_d:

- For Ox720 with literature[a,b]
- Relative scaling[c]: Ox720 > NB > CV

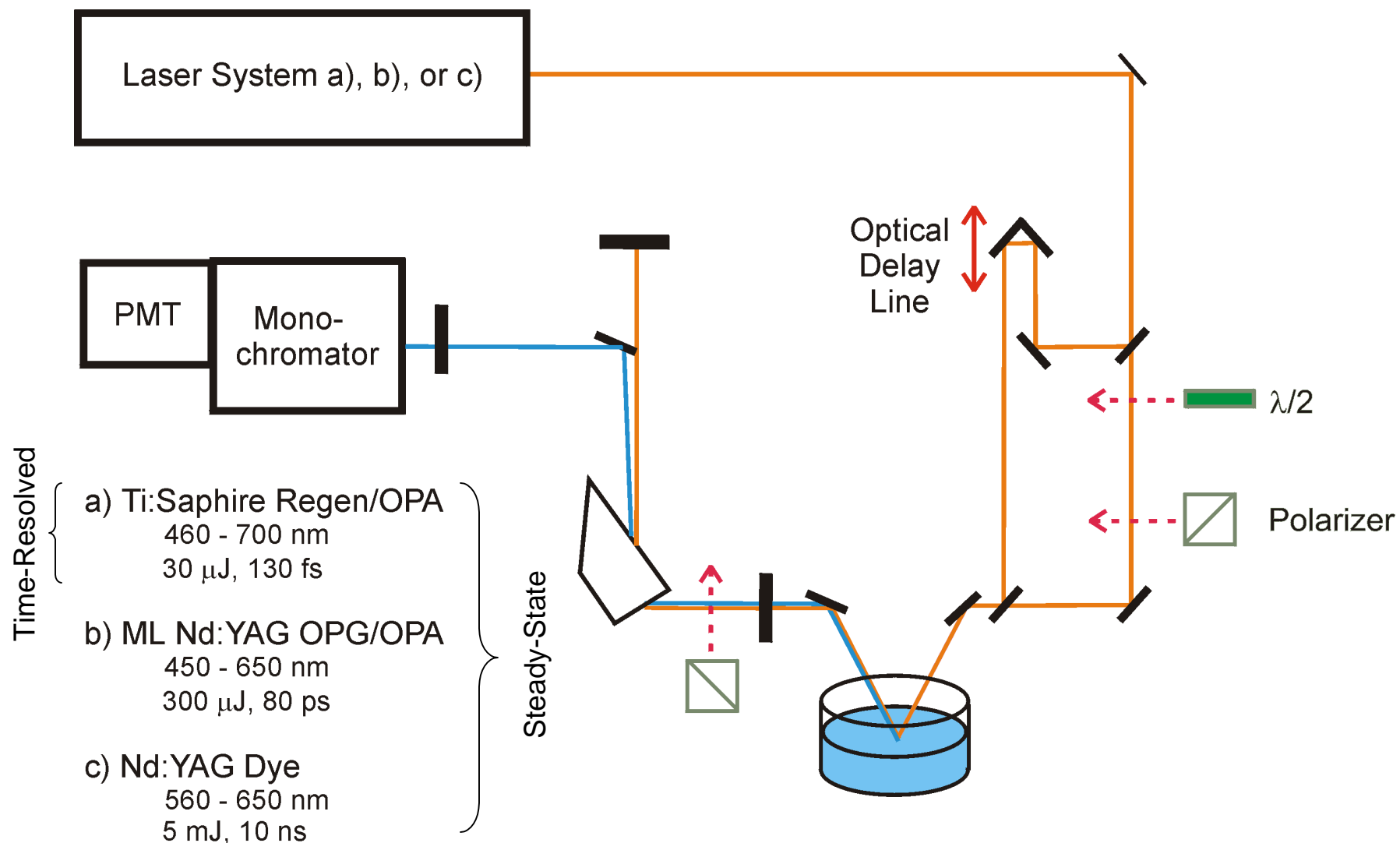Adding salt increases dimer concentration ($1/K_d$) by factor of 2 - 3

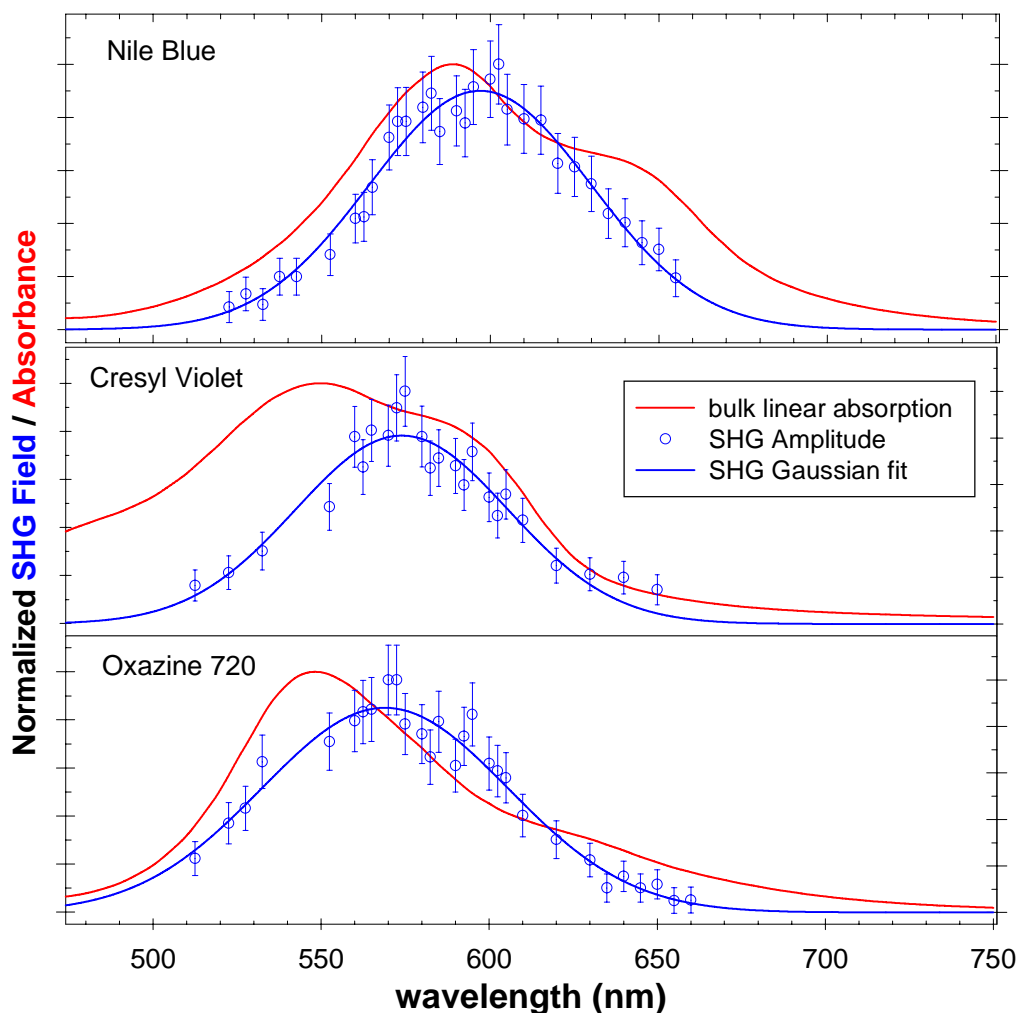|	**Oxazine dyes in water: Peak positions and K_d**		
Dye	λ_{max} **(monomer)** (nm)	λ_{max} **(dimer)** (nm)	**$1/K_d$** (M^{-1}) ($\pm$ 30%)
oxazine 720	620	570	50,000
			50,000[a]
			10,000-100,000[b]
Nile blue	630	590	10,000
cresyl violet	580	550	3200

[a] Gvishi & Reisfeld, 1989   [b] Herkstroeter et al., 1990   [c] Morozova and Zhigalova, 1982

SHG Interface Studies

SHG Spectra of Oxazines at Air/Water Interface

- One band in SHG spectra single species

- SHG(ω): resembles input resonance (at ω) more than output (at 2ω)

- SHG peaks are slightly red-shifted

- Red-shift previously reported for dye dimers at air / solid interface (Kemnitz & Leach): intermolecular interactions rather than a more polar interface

- Interface polarity has been found to be average of two bulk phases (Eisenthal)
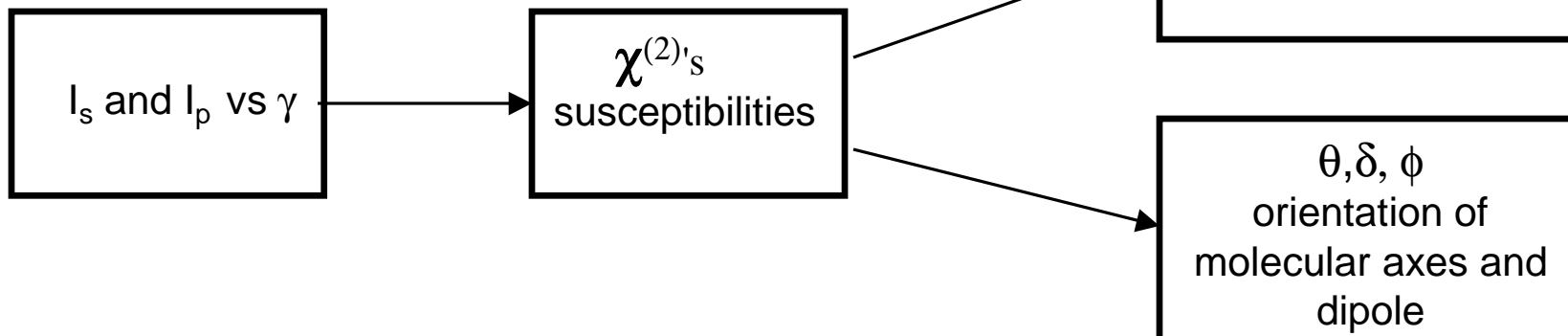
SHG Polarization Dependence and Orientation

Input (γ) and output polarization resolved I_{SHG}

- Orientational information
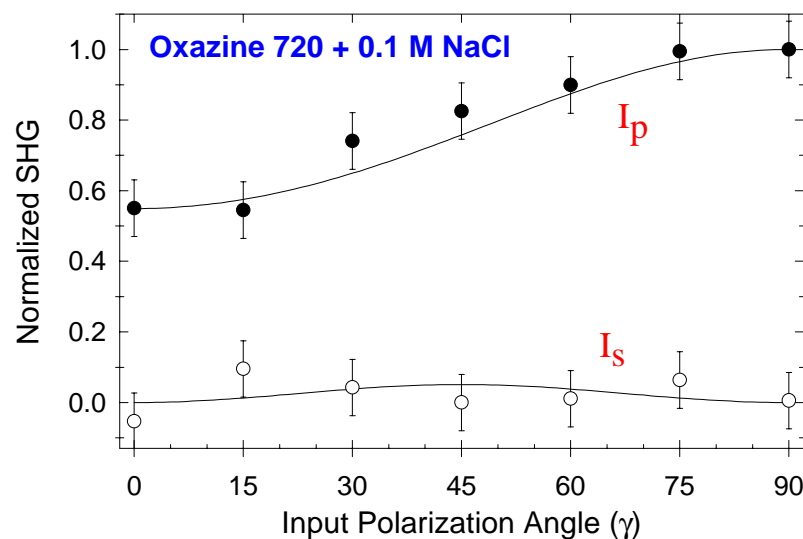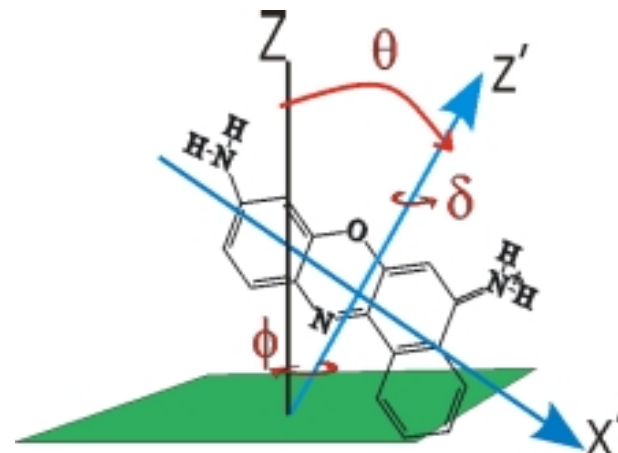- SHG dependence:

  concentration or orientation?
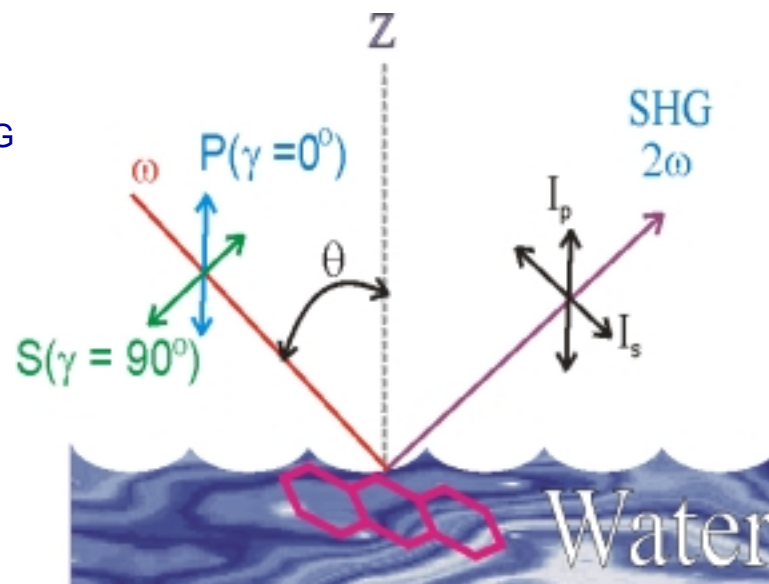
Methods extensively developed and used

$$\chi_{IJK} = N_s \Sigma <T_{IJKijk} (\theta, \delta, \phi)> \beta_{ijk}$$

```
┌─────────────────┐      ┌─────────────────┐      ┌─────────────────────┐
│                 │      │    χ(2)'s        │      │     β's             │
│ Is and Ip vs γ  │─────▶│ susceptibilities │─────▶│ hyperpolarizabilities│
│                 │      │                  │      └─────────────────────┘
└─────────────────┘      └─────────────────┘
                                  │           ┌─────────────────────┐
                                  │           │     θ,δ, φ          │
                                  └──────────▶│ orientation of       │
                                              │ molecular axes and   │
                                              │ dipole               │
                                              └─────────────────────┘
```

Results from SHG Polarization Dependence/Anisotropy

	[NaCl] (M)	$\delta = 45^0$, random θ $(^0)$
Nile blue	0	17.2
	0.01	20.3
oxazine 720	0	23.4
	0.1	22.5
cresyl violet	0	26.0
	0.1	24.5

Oxazine 720 + 0.1 M NaCl

I_p

I_s

Normalized SHG

Input Polarization Angle (γ)

Similar results for all dye samples:

- **Little or no detectable orientation variation**
- **I_{SHG} vs. solution composition: [Dimer] not orientation!!!**

Steady-State SHG of Oxazine Dyes

Results from several measurements:

SHG Only from Dimers at Surface

- Single band in spectra

- Orientation independent of coverage

- I_{SHG} consistent with bulk aggregate behavior
  - Increases with salt concentration
  - No SHG from
    - Methanolic and surfactant solutions
   - Non-aggregating oxazines

Interface effects vary with property:

- Dimer preference at water surface
  - Surface less polar than bulk - average of bulk phases (Eisenthal)
  - Our measurement of ΔG_{ads} also consistent with lower polarity

- Red-shifted spectra
  - Could be intermolecular interactions of dyes

Aggregates at the interface are a sensitive probe of surface effects!

Ultrafast Studies of Oxazines at Air/Water

**Previous ultrafast work on:**

- **Dyes in solution**   Solvation dynamics - mature field
- **Aggregates**   Mostly thin film / monolayer and J-aggregates
- **Liquid interfaces**   Rotational dynamics & isomerization
- **Oxazines**   CV, NB on SiO_2 and SnO_2 nanoparticles (Kamat)

    # of decay times: One for insulators

    Two for semiconductors (back ET)

S_1 ————

S_o ————

monomer

$h\nu$

S_1^+

IC_1

S_1^-

T_1

IC_2

S_o

dimer
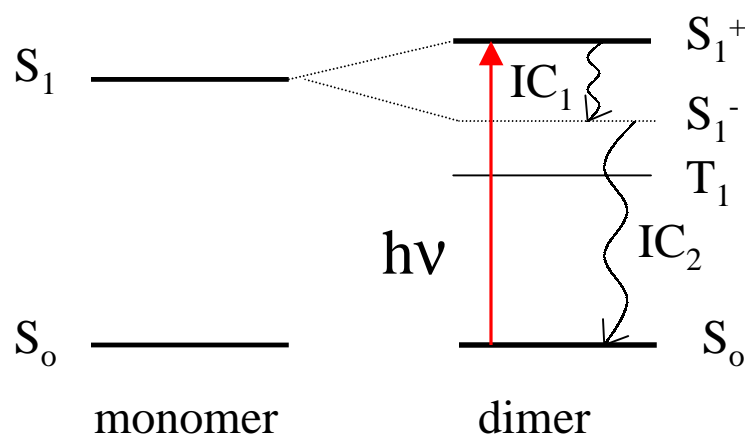
Initial internal conversion -
$S_1^+ \rightarrow S_1^-$ (IC_1): <100 fs
Fluorescence not observed

Resolved time:
$S_1^- \rightarrow S_0$ (IC_2 or k_{nr})
    CV: 2.5 ps
    NB:<20 ps

Transient Absorption in **Solution**

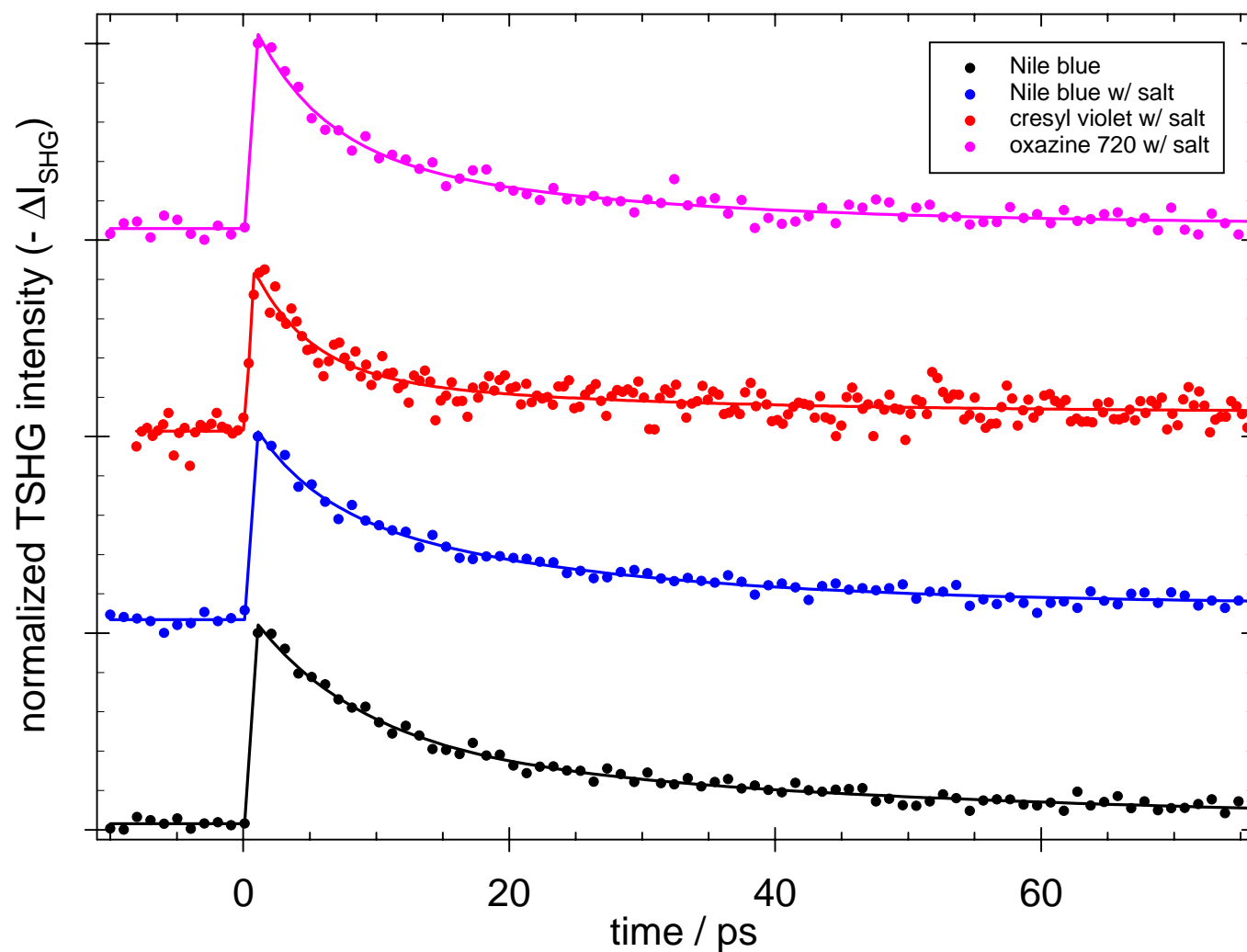Nile blue 580 nm pump / continuum probe
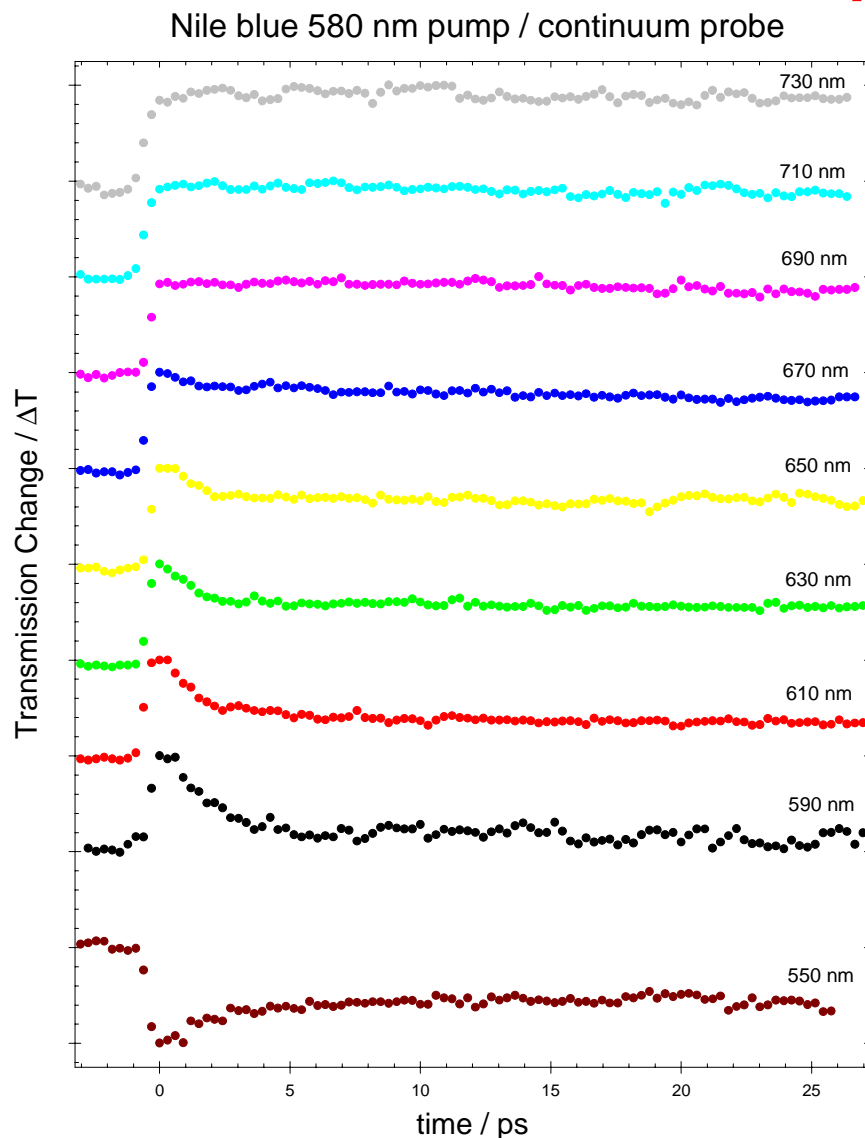
Results can be described in terms of well-known mechanisms:

- Time-Resolved Stokes shift due to solvation dynamics, delayed red shift

- Excited-state lifetimes in water (τ_f), (literature)

  - o NB: 420 ps
  - o Ox720: 1.8 ns
  - o CV: 3.3 ns

- No evidence of signals from bulk dimers

Ultrafast TSHG at the Air/Water Interface
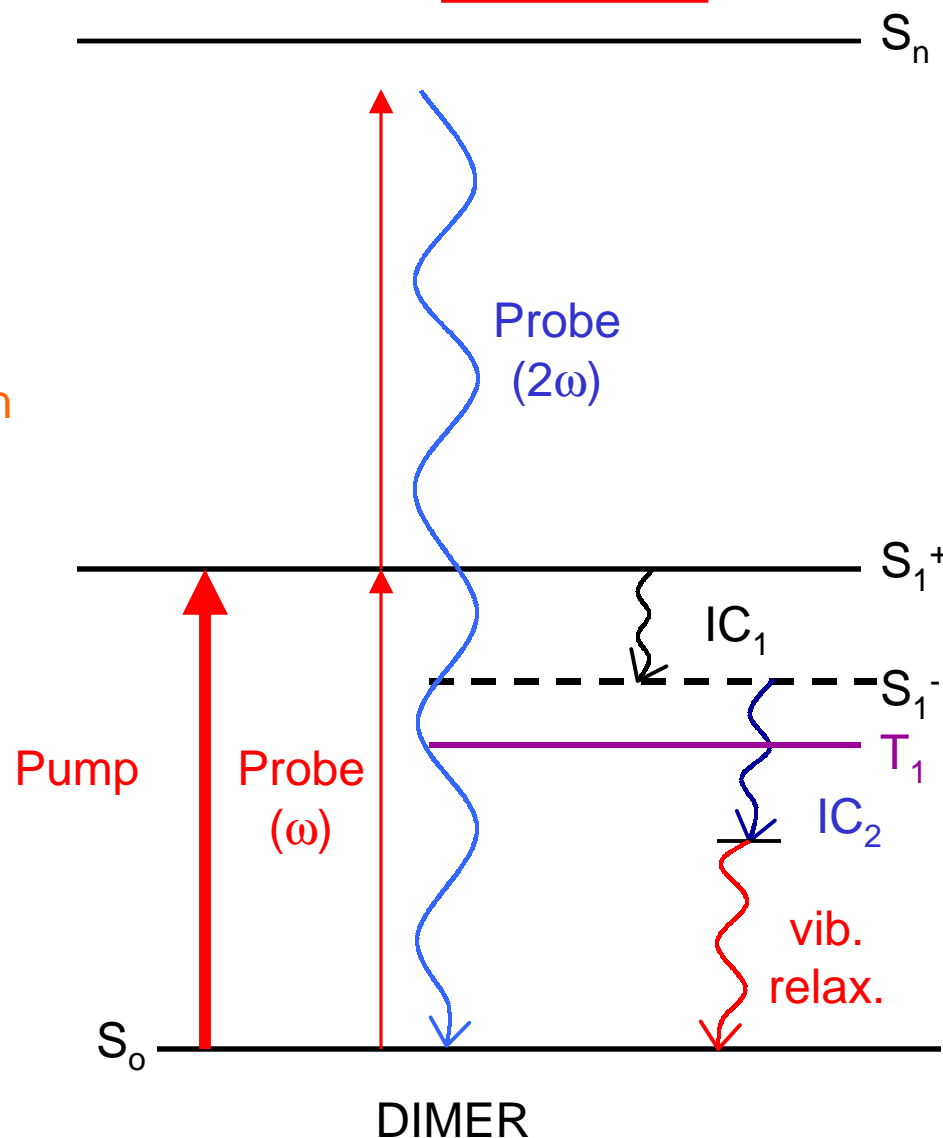
580 nm pump - SHG (290 nm) probe

Ultrafast TSHG at the Air/Water <u>Interface</u>

580 nm pump - SHG (290 nm) probe

- Single-photon resonant SHG

- Two parallel GSR mechanisms
  - o Ground state solvent relaxation
  - o Vibrational relaxation of hot ground state aggregates

TSHG decay times for aqueous oxazine dye solutions.

dye	τ_1 ($\pm$15%) ps	τ_2 ($\pm$15%) ps
OX720	5	23
CV	4	23
NB	5	22
NB w/o LiCl	8	44

S_n

Probe (2ω)

S_1^+

IC_1

S_1^-

T_1

IC_2

Pump

Probe (ω)

vib. relax.

S_o

DIMER

Conclusions

Are interfacial properties consistent with the idea of averaging bulk values?

- **Some are:**
  - Dominance of dimer at surface due to
    - Dyes driven to lower polarity (hydrophobicity)
    - Interface polarity is the average of the values for water and air
- **Others are not:**
  - Red-shifted dimer SHG spectrum
  - Relative I_{SHG} and K_d vs. bulk salt concentration

Oxazine TSHG dynamics at the interface are:

- **Different** than the bulk
- New intermediate decay times are similar to previous aggregate results
  - Transient due to ground state recovery
    - Single-photon resonant SHG signal
    - Biexponential recovery
- Observed additional recovery compared to colloidal SiO_2 / water interface

Acknowledgements

References:

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